

# Formation of Carbon and Hydrogen Species in Magmas at Low Oxygen Fugacity

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*Studies of iron-bearing silicate melt (ferrobasalt) + iron metallic phase + graphite + hydrogen equilibria show that carbon and hydrogen solubilities in melts are important for the evolution of the upper mantle. In a series of experiments conducted at 3–7 GPa and 1520–1600°C, we have characterized the nature (oxidized vs reduced) and quantified the abundances of C- and H-compounds dissolved in iron-bearing silicate melts. Experiments were carried out in an anvil-with-hole apparatus permitting the achievement of equal chemical potentials of H<sub>2</sub> in the inner Pt capsule and outer furnace assembly. The  $fO_2$  for silicate melt–iron equilibrium was  $2.32 \pm 0.04$  log units below iron–wüstite (IW). The ferrobasalt used as starting material experienced a reduction of its iron oxides and silicate network. The counterpart was a liberation of oxygen reacting with the hydrogen entering the capsule. The amount of H<sub>2</sub>O dissolved in the glasses was measured by ion microprobe and by step-heating and was found to be between 1 and 2 wt %. The dissolved carbon content was found to be 1600 ppm C by step-heating. The speciation of C and H components was determined by IR and Raman spectroscopy. It was established that the main part of the liberated oxygen was used to form OH<sup>−</sup> and to a much lesser extent H<sub>2</sub>O, and only traces of H<sub>2</sub>, CO<sub>2</sub> and CO<sub>3</sub><sup>2−</sup>. Dissolved carbon is mainly present as atomic carbon or amorphous carbon. It was possible to measure an isotopic fractionation of 0.8‰ between graphite and dissolved or amorphous carbon at the temperatures of experiments. The Raman spectra also suggest that the network units might contain Si–C bonds. Comparison of our results with the literature demonstrates that the amount of dissolved species decreases as  $fO_2$  decreases. In the light of these experimental data, it appears that large-scale melting of the proto-Earth could be associated with*

*melts containing an oxidized form of hydrogen. The early Earth, however, was likely to have been a very reducing environment, in which most of the carbon remained stable in the form of graphite. As the Earth became more and more oxidized, melts formed at depth would have dissolved larger amounts of water, and also carbon in the form of CO<sub>2</sub>, which would have made the degassing of the upper mantle more and more efficient.*

KEY WORDS: ferrobasalts; experimental petrology; oxygen fugacity; stable isotopes

## INTRODUCTION

It is generally accepted that most of the present-day upper mantle is moderately oxidized at oxygen fugacities well above metal saturation. The application of olivine–orthopyroxene–spinel phase equilibrium methods to measure the oxygen fugacity ( $fO_2$ ) at which upper-mantle peridotites equilibrated has led to the consensus that the lithospheric upper mantle is, nearly everywhere, relatively oxidized, the majority of samples falling within −3 to +1 log units (bars) of the fayalite–magnetite–quartz oxygen buffer ( $\Delta FMQ = -3$  to +1) (Wood *et al.*, 1990; Ballhaus, 1993). Fluids identified in mantle samples are also oxidized, and consist mainly of CO<sub>2</sub> + H<sub>2</sub>O. So far, the most reduced samples from cratonic Archean lithosphere plot as low as  $\Delta FMQ = -3$  to −5 (Mattielli

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*et al.*, 1989; Wood *et al.*, 1990; Daniels & Gurney, 1991; Ballhaus, 1993; Kadik, 1997; Parkinson & Arculus, 1999). These low  $f\text{O}_2$  values are considered to provide evidence that the upper mantle was originally more reduced and has become progressively more oxidized with time (e.g. Arculus, 1985), and that at least part of the upper mantle is reduced enough to stabilize carbon and  $\text{CH}_4$  at depth. One consequence of this observation is that even the parts of the upper mantle at the lower end of the recorded range have  $f\text{O}_2$  values 2–3 log units more oxidized than that appropriate for chemical equilibrium with an Fe-rich metallic phase (O'Neill & Wall, 1987). If the average mantle olivine ( $\text{Fo}_{91}$ ) was in chemical equilibrium with core-forming iron, the  $f\text{O}_2$  would be at least 5 log units more reduced than the present-day upper-mantle value.

It has been argued that the composition and oxidation state of the mantle is the result of heterogeneous accretion with more than one core-forming event as proposed by Arculus *et al.* (1990), with the addition of an oxidized 'late veneer' (Wanke, 1981; Javoy, 1997), or of an auto-redox process in the upper mantle (O'Neill, 1991; Javoy, 1995; Galimov, 1998). O'Neill & Pownceby (1993), Ballhaus (1995) and Wood (1995) have proposed that the present-day mantle becomes more reduced with increasing depth. Crystal-chemistry considerations (molar volume effect, changes in solid solution, phase transitions and the incorporation of  $\text{Fe}^{3+}$  in the spinelloid phases) require that  $f\text{O}_2$  declines with respect to the FMQ buffer as depth increases. This suggests that the convecting upper mantle may become saturated with an Fe-dominated metal phase at a depth of around 300 km.

Although the oxidized nature of the upper mantle is still subject to debate, it is plausible that the relative abundances of H and C species under reduced conditions play an important role in partial melting of the present-day mantle as a whole. However, the nature of mantle partial melting under reduced conditions in the presence of graphite and C–O–H volatiles is still not clear. The following studies have investigated different synthetic systems in the presence of reduced volatiles: Egglar & Baker (1982) examined the effect of C–H volatiles on melting of the diopside ( $\text{Di}_{35}$ )–pyrope ( $\text{Py}_{65}$ ) system at 20 GPa and  $f\text{O}_2$  near the Si– $\text{SiO}_2$  buffer; Taylor & Green (1987) explored the system nepheline–forsterite–silica–methane-dominated fluid at 2.8 GPa, 1300°C and  $f\text{O}_2$  at IW – 5 (where IW is the iron–wüstite buffer); Holloway & Jakobsson (1986) measured the solubility of  $\text{CO}_2$ , CO,  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$  in silicate melts at 1–2 GPa, 1200°C where the C–O–H phase was buffered by graphite, iron and wüstite; Luth *et al.* (1987) studied the  $\text{H}_2$  solubility in melts of  $\text{NaAlSi}_3\text{O}_8$  composition; and Holloway *et al.* (1992) and Kadik (1996) considered the dissolution of free carbon (graphite) in basaltic melt at variable pressure and  $f\text{O}_2$ . Holloway & Jakobsson (1986) and Taylor &

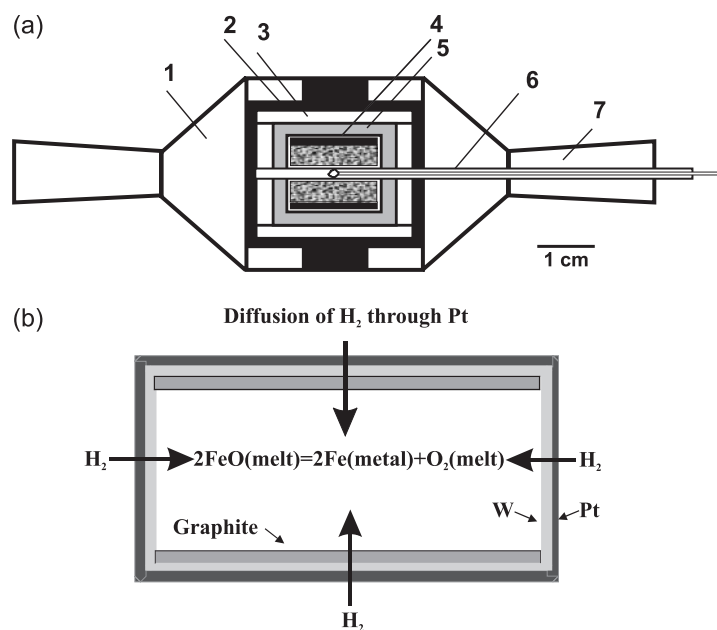
Green (1987) have shown that low  $f\text{O}_2$  produces a general reduction of the silicate network, with C–H species dissolved as  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , and  $\text{CO}_3^{2-}$ . Dissolution of free carbon may be the source of  $\text{CO}_3^{2-}$  (Holloway *et al.*, 1992) or  $\text{C}^{2-}$  in melt (Swisher, 1968). It is expected that interaction of carbon and its volatile compounds with a silicate melt strongly depends on  $f\text{O}_2$ , correspondingly changing the forms of its stability in silicate liquids to  $\text{CO}_2$ ,  $\text{CO}_2^{3-}$ , Si–C, and C–Me (Ca, Mg, Fe). Nevertheless, these specific features of carbon dissolution in many ways remain unclear.

In this paper, our major concern is to look at the speciation and concentration of carbon and hydrogen when they dissolve in a melt, and the possible implications for upper-mantle evolution. We will show the role that melting of a reduced carbon-bearing upper-mantle source plays in the generation of oxidized C–O–H volatiles. The model for the Earth's formation proposed by Javoy (1995, 1997, 1999) is based, among other features, on the equivalence of the oxygen isotopic composition of enstatite chondrites (EH) with that of the Earth and Moon. More than 99% of the Earth could be formed from such meteoritic parental material, and the balance by a late veneer of carbonaceous chondrite (CI) or comet-like material. The proto-Earth (formed from pure EH) could host about 50% of the final carbon content of the present Earth and only 6% of the hydrogen, and would have been very reduced ( $f\text{O}_2$  IW – 3 to IW – 5). It would have contained very little or no oxidized iron, only reduced forms of carbon and almost no water. Core formation induced by the major impact during the creation of the Moon initiated nearly complete melting of the mantle. The upper mantle left after the main core-forming iron extraction event would still have been reduced and contained more iron than the present upper mantle, and a carbonaceous phase such as graphite, diamond or carbide. The Earth would still have been hot, and Fe-rich magmas probably existed. The late veneer brought 94% of the hydrogen and about 50% of the carbon (in the form of hydrous minerals, complex hydrocarbon molecules and carbonates). The recycling of the late veneer is the source of the oxygen needed to reach the level of oxidation of the proto-mantle. Our study of the system graphite–ferrobasalt at low  $f\text{O}_2$  (IW – 2 to IW – 3), 3.7 GPa and 1520–1600°C is an attempt to model experimentally, with more details than previous work, the equilibrium between oxidized and reduced forms of C- and H-components present in a melt formed under reduced conditions.

## HIGH-PRESSURE EXPERIMENTS

### Experimental techniques

Experiments were carried out in an anvil-with-hole apparatus at 3.7 GPa, 1520–1600°C and controlled



**Fig. 1.** The experiment at reducing conditions. (a) Schematic representation of the anvil-with-hole apparatus: 1, container (lithographic limestone); 2, heater (high-purity graphite); 3, sample holder (MgO: BN<sub>hex</sub> = 3:1, weight ratio); 4, sealed Pt capsule lined with W foil; 5, buffer mixture (pressed Fe<sub>2</sub>O<sub>3</sub>); 6, thermocouple, Pt + 30%Rh/Pt + 6%Re; 7, ceramic sleeve. (b) Schematic regime of H<sub>2</sub>. An experiment under reducing conditions includes the following stages: 1, H<sub>2</sub> diffusion into the platinum capsule from the buffer assemblage; 2, formation of Fe alloy and liberation of O<sub>2</sub>; 3, interaction of H and O with melts and graphite, formation of an 'oxidized bond' and 'reduced bond'.

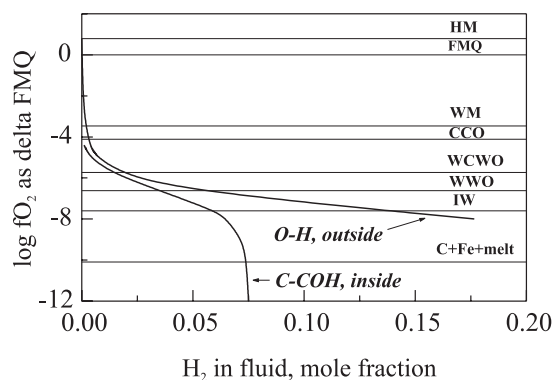
hydrogen (oxygen) activity as described by Litvin (1989). The device is a 2000 tons uniaxial press, equipped with a high-pressure system consisting of a pair of tungsten carbide anvils with holes and a cell (Fig. 1a). Each hole is a truncated cone. Two anvils are axially and oppositely directed, separated by pyrophyllite gaskets. They form a cavity that holds the sample assembly. The space inside the heater is 6 cm<sup>3</sup>, and characterized by a uniform distribution of temperature ( $\pm 5^\circ\text{C}$ ) and pressure ( $\pm 0.1$  GPa). The sample is placed in a sealed Pt capsule 10 mm in diameter and 5 mm in height. Two capsules of this type are used in one assembly. The temperature is measured by a Pt30%Rh/Pt6%Rh thermocouple in a radial position, with its junction in the centre of the cell assembly (between the capsules). The accuracy of temperature measurements is  $\pm 5^\circ\text{C}$  at 1500°C and close to  $\pm 10^\circ\text{C}$  at 1600°C. Pressure is determined at room temperature with Bi-based transducers incorporated in each cell assembly. Pressures at high temperatures were calibrated using the quartz–coesite transition (Bohlen & Boettcher, 1982). The reproducibility of experimental pressures in the cell assembly is estimated as  $\pm 0.1$  GPa.

Silicate composition in the ferrobasalt–graphite system was prepared from a natural basaltic rock (in wt %: Na<sub>2</sub>O 2.68, MgO 4.98, Al<sub>2</sub>O<sub>3</sub> 13.12, SiO<sub>2</sub> 49.18, K<sub>2</sub>O 0.36, CaO 8.40, TiO<sub>2</sub> 1.95, MnO 0.28, FeO 18.01, P<sub>2</sub>O<sub>5</sub> 0.22). Starting materials were powdered glasses. Samples were melted in the presence of N<sub>2</sub> at 1250°C in alundum crucibles, and quenched in air to colourless glasses; their

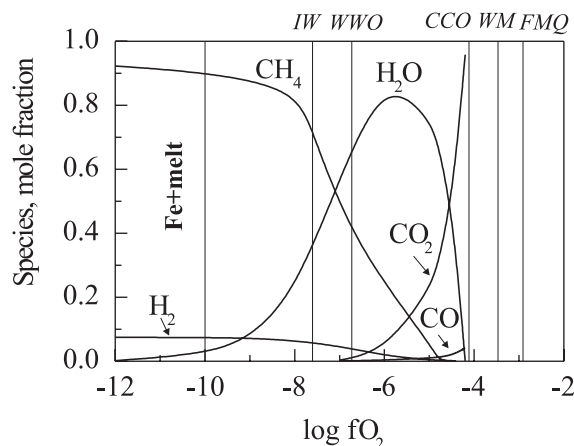
composition and homogeneity were checked by microprobe analysis. The charges consisted of 200–300 mg of powdered glass topped by a graphite disc 0.2 mm thick (Fig. 1a). They were isolated from the Pt capsule walls by tungsten foil (0.05 mm thick), which reduces the interaction between the Fe-bearing melt and platinum (Litvin, 1989). The run duration varied between 30 and 120 min at 1500–1600°C. The experiments were quenched by turning off the power. The initial quench rate was  $\sim 200^\circ\text{C/s}$ .

### Regime of hydrogen and oxygen fugacity

The technique of  $f\text{O}_2$  buffering employed here relies upon the diffusion of H<sub>2</sub> through Pt to achieve equal chemical potentials of H<sub>2</sub> in the inner Pt capsule and outer solid  $f\text{O}_2$  buffer assembly in the presence of H<sub>2</sub>O. Ulmer & Luth (1991) used a similar method to investigate graphite–C–O–H fluid equilibria. In the case of our experiments the  $f\text{H}_2$  was buffered by the furnace assembly functions at the iron (Fe)–wüstite (FeO) buffer. Under such conditions, the  $f\text{H}_2\text{O}/f\text{H}_2$  ratio in the O–H system is fixed at a given pressure and temperature. The  $f\text{O}_2$  imposed on the charge by graphite is controlled by the equilibrium between graphite, H<sub>2</sub> buffered externally, and the reduction of the Fe-bearing melt with liberation of O<sub>2</sub> (Fig. 1b). If a C–O–H fluid is present, the  $f\text{O}_2$  (Fig. 2) and the C–O–H fluid composition (Fig. 3) would correspond to the equilibrium values in a C–O–H system at a given  $P$  and  $T$ . A feature of our experiments



**Fig. 2.** The relative oxygen fugacity (with respect to FMQ buffer) of a separate C–O–H fluid in equilibrium with elemental carbon plotted against the  $H_2$  mole fraction in the fluid at 40 kbar and 1500°C. Also shown is the position of solid-state buffers: fayalite–magnetite (FMQ), magnetite–haematite (HM), wüstite–magnetite (WM) and iron–wüstite (IW) (Chou, 1987). The upper elemental carbon stability limit is given by the equilibrium  $C + O_2 = CO_2$  (CCO). The upper stability limit of the tungsten foil and WC is given by the equilibria  $W + O_2 = WO_2$  (WWO) and  $WC + O_2 = WO_2 + C$  (WCWO) (O'Neill & Pownceby, 1993; Taylor & Foley, 1989). Calculated values (see text) of the  $fO_2$  values for ferrobaltic melt + graphite + iron equilibrium (C + Fe + melt) during experiments at 3.7 GPa and 1520–1600°C are shown.



**Fig. 3.** The  $fO_2$  values of a C–O–H fluid in equilibrium with graphite with  $fH_2$  imposed by H–O equilibrium outside a Pt capsule at 4 GPa and 1500°C. The C–O–H equilibrium has been calculated using the modified Redlich–Kwong formulation (MRK) (Holloway, 1981). Oxygen buffers are shown for reference and are labelled as in Fig. 2.

is that they were carried out under C–O–H fluid-absent conditions (inside the capsules), verified by the absence of bubbles at any observable scale. In theory, the  $fO_2$ , which corresponds to the phase equilibrium during the experiments, is dominated by the reaction



corresponding to the reduction of an iron-bearing melt under the influence of  $H_2$  diffusion through Pt. Calculations demonstrate that, at a given  $fH_2$  in the system, the  $fO_2$  of a C–O–H-bearing melt inside the Pt

capsule should be much lower than the  $fO_2$  of an O–H fluid phase outside the Pt capsule (see Fig. 2 and figure caption for details).

### Oxidation state of the C–O–H-bearing glasses after the experiment

Metal–silicate partition coefficients depend strongly on  $fO_2$  (see, e.g. Hillgren *et al.*, 1994). Normally the  $fO_2$  of such experiments is calculated based on a calibration of the IW buffer along with the concentrations of FeO in the silicate and of Fe in the metal [see equation (1)].

The equilibrium constant for reaction (1) is

$$\log K = \log (a_{FeO}/a_{Fe}) - \frac{1}{2} \log fO_2^{exp} \quad (2)$$

where  $\log fO_2^{exp}$  is the  $fO_2$  of the high-pressure experiment. The equilibrium constant for the reaction between pure Fe and pure FeO (which defines the IW buffer), with  $a_{Fe} = 1$  and  $a_{FeO} = 1$ , reduces to

$$\log K = -\frac{1}{2} \log fO_2^{IW} \quad (3)$$

where  $\log fO_2^{IW}$  gives the oxygen fugacity of the Fe–FeO equilibrium under the  $P$ – $T$  conditions of the experiment.

The  $fO_2$  of the experiment may also be expressed relative to the IW buffer curve:

$$\log fO_2^{exp} = \log fO_2^{IW} - \Delta IW \quad (4)$$

where  $\Delta IW$  is the difference between  $\log fO_2^{IW}$  and the  $fO_2$  of the experiment ( $\log fO_2^{exp}$ ). Combining equations (2), (3) and (4) gives

$$\log (a_{FeO}/a_{Fe}) - \frac{1}{2} (\log fO_2^{IW} - \Delta IW) = -\frac{1}{2} \log fO_2^{IW} \quad (5)$$

and thus

$$2 \log (a_{FeO}/a_{Fe}) = \Delta IW \quad (6)$$

where  $a_{FeO}$  and  $a_{Fe}$  are the activities of FeO and Fe in iron-bearing melt and metal, respectively. Inserting the respective activities of Fe and FeO in the product phases into equation (6) thus allows the  $fO_2$  to be determined relative to the Fe–FeO equilibrium. The activity coefficient for FeO in the melt at 1520–1600°C was calculated from Ariskin *et al.* (1993). The  $fO_2$  for the melt–iron equilibrium yields an  $fO_2$  of 2.26–2.37 log units below IW ( $\Delta \log fO_2^{IW} = -2.37$  for Fb148-gl,  $\Delta \log fO_2^{IW} = -2.33$  for Fb150-gl and  $\Delta \log fO_2^{IW} = -2.26$  for Fb231-gl).

## RESULTS

Three runs were completed at 3.7 GPa in a narrow range of temperature (1520–1600°C) and  $\Delta \log fO_2^{IW} = -2.32 \pm 0.06$ . The experimental conditions of each run are given

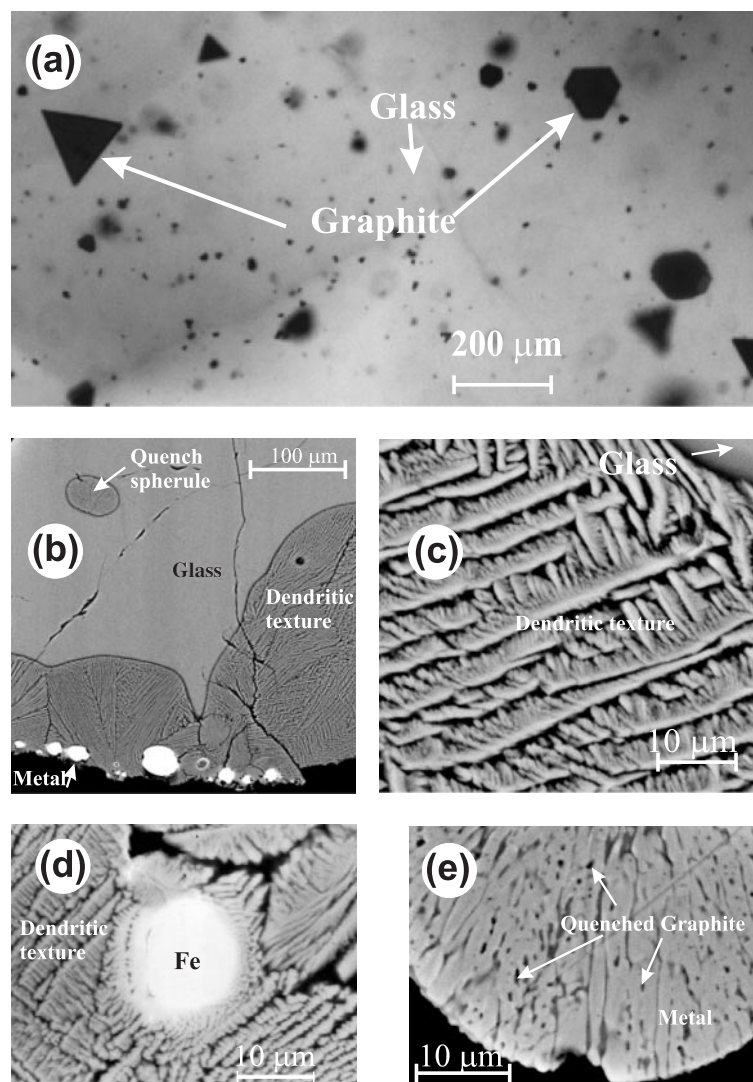
Table 1: Electron microprobe analyses of run products: clear glass, glass with quench dispersed graphite (C) and Fe alloy after experiments at 3.7 GPa, 1520–1600°C

Sample	Quench product		Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	FeO	P <sub>2</sub> O <sub>5</sub>	Total
Glass													
Fb148-gl	Clear glass	Average (5)	2.83	5.31	13.36	52.34	0.34	9.17	2.24	0.26	10.22	0.11	96.55
		SD	0.05	0.09	0.47	1.07	0.02	0.19	0.07	0.03	0.18	0.02	1.64
Fb148-bl	Glass + quench C	Average (3)	2.89	5.09	14.44	53.22	0.39	8.96	2.05	0.25	10.41	0.14	97.90
		SD	0.00	0.19	0.24	0.44	0.00	0.12	0.15	0.07	0.06	0.02	1.15
Fb150-gl	Clear glass	Average (8)	2.89	5.34	13.91	53.30	0.38	9.19	2.15	0.24	11.26	0.18	98.99
		SD	0.05	0.08	0.25	0.55	0.01	0.11	0.08	0.02	0.19	0.05	0.49
Fb150-bl	Glass + quench C	Average (3)	2.96	4.84	13.95	52.46	0.30	9.59	2.26	0.28	13.17	n.d.	99.81
		SD	0.17	0.09	0.21	0.95	0.02	0.25	0.07	0.06	1.03		0.52
Fb231-gl	Clear glass	Average (5)	2.80	5.04	13.74	52.21	0.37	8.89	2.07	0.29	11.73	0.18	97.44
		SD	0.08	0.14	0.09	0.49	0.01	0.06	0.04	0.02	0.28	0.03	0.83
Fb231-bl	Glass + quench C	Average (5)	2.78	4.90	13.97	53.29	0.28	9.42	2.16	0.3	12.04	0.18	99.32
		SD	0.08	0.17	0.10	0.65	0.03	0.25	0.07	0.08	0.51	0.03	0.08
Sample	Quench product		Fe	Co	Ni	Si	P	W	Pt	Total			
Fe alloy													
Fb148-gl	Spherical droplet	Average (5)	91.30	0.16	0.08	0.17	0.99	4.93	0.99	97.62			
		SD	1.27	0.02	0.03	0.07	0.38	0.79	0.38	0.72			
Fb150-gl	Spherical droplet	Average (5)	87.85	0.17	0.08	0.27	0.71	2.35	0.04	91.47			
		SD	0.99	0.02	0.04	0.11	0.22	0.96	0.04	0.50			
Fb231-gl	Spherical droplet	Average (3)	89.74	0.19	0.10	0.08	1.25	0.10	0.13	92.45			
		SD	1.48	0.01	0.05	0.02	0.14	0.09	0.18	0.89			

in Table 1. The recovered charges were examined microscopically under reflected light using immersion oil. The charges consist of pink glasses containing spherical droplets of metallic iron concentrated at the bottom of the charge (30–100 µm in size) and thin hexagonal and triangular tablets of graphite crystals (100–300 µm in size) visible in transmitted light (Fig. 4a). No bubbles were visible. The charges were studied by a series of techniques to tentatively characterize the form in which carbon and hydrogen were present and their speciation. These techniques included: (1) electron microprobe to visualize the texture and to acquire compositional data for the various phases present; (2) IR spectroscopy to characterize H- and C-species detectable by this technique; (3) Raman spectroscopy, which allowed the characterization of poorly crystallized graphite (which could not be detected by the preceding technique) and the possible presence of Si–C, and further checks for the presence of the OH<sup>−</sup> bond; (4) ion probe analysis to measure the amount of hydrogen present in the glasses to compare with the step-heating technique (5); (5) step-heating to quantify the amount of water and carbon present in the glass phases and to look at isotopic fractionation between graphite and the dissolved carbon.

### Electron microprobe analysis

Electron microprobe analysis of glasses and iron-rich globules was performed at the Microprobe Camparis Centre of the Université de Paris, with an SX50 Cameca microprobe, four wavelength-dispersive spectrometers (WDS) and one energy-dispersive spectrometer (EDS). At the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences (Moscow), we used a Camebax microbeam and four wavelength-dispersive spectrometers (WDS) and one energy-dispersive spectrometer (EDS). Polished epoxy mounts containing the samples were coated with carbon. The images obtained by electronic microscopy show that the silicate liquid was not quenched to a glass at the top and bottom parts of the charges, but crystallized dendritically and formed spheroids (50–200 µm in size) as inclusions in clear glass (Fig. 4b–d). The metallic Fe-rich globules are spherical with a dendritic microstructure (Fig. 4d and e), which suggests that this phase was liquid during the experiment. Selected analyses of the phases (clear glasses, glass containing dendritic texture) are given in Table 1. Each glass composition represents at least five analyses. For the glass from the quenched zone, the beam



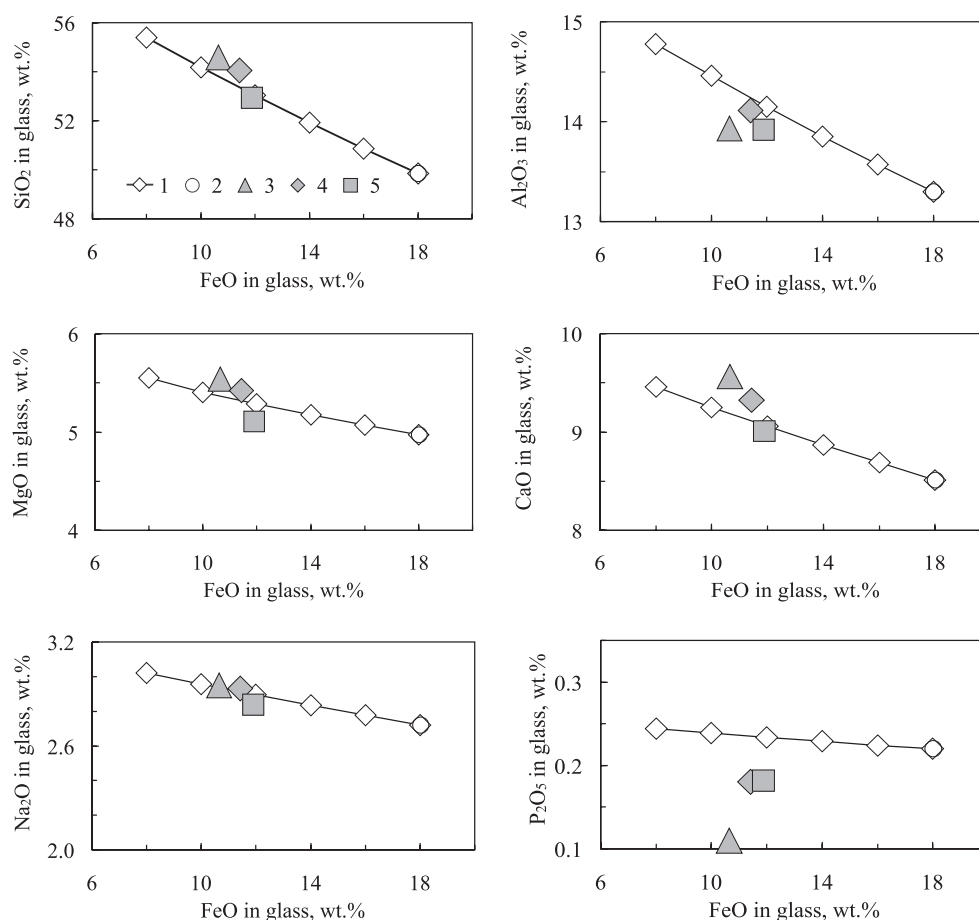
**Fig. 4.** (a) Optical photomicrograph of the run products in fb148-glass, transmitted light. Thin hexagonal and triangular black tablets are graphite crystals equilibrated with melt. (b)–(e) Backscattered electron photographs of run products (Run 148). (b) Contact between glass (light grey) and the bottom parts of samples with a quenched dendritic microstructure. Dark spheroids in the clear glass are inclusions with a quenched dendritic texture. Bright spherical droplets are the iron metallic phases largely segregated in the bottom region of the charges. Dark area is epoxy. (c) Detailed view of the dendritic texture of the glass and the quench dispersed graphite. (d) Quench dendritic microstructure around metallic iron. (e) Quench graphite dendritic texture within metallic Fe droplets.

was defocused to minimize specimen damage. The fact that a similar chemical composition was found for both clear and dendritic textures indicates that such textures are linked to quenching.

The main feature of the chemical compositions is the decrease of FeO concentration from 18 wt % (FeO content of the starting material) to 10.2–11.7 wt % FeO. This phenomenon reflects reduction of some of the FeO in the starting melts to Fe metal (6.48 wt % Fe for Fb148-gl, 5.85 wt % Fe for Fb150-gl and 5.46 wt % Fe for Fb231-gl). Figure 5 shows melt compositions calculated assuming that part of the reduced FeO has been removed. Comparison of these estimates with the

glass compositions (normalized to 100%) demonstrates that the crystallization of Fe is responsible for the melt composition changes.  $P_2O_5$ , however, shows much lower contents than those calculated. This is explained by the solubility of P in Fe-phases (0.7–1.25 wt %) and their following simultaneous removal. The Fe contents of the tungsten foils and the Pt capsule are below 0.1 wt %. The contents of Pt in W and W in Pt are also very low (below 0.01–0.1 wt %). Measurement of the samples revealed that, for both metals, the total sum of Pt and W averaged around 99.8%. The iron-rich globules were analysed and compared with known iron–carbon alloys, which allowed the carbon





**Fig. 5.** Compositional variation of C–H-bearing glasses vs wt % FeO as an indicator of the degree of melt reduction. The SiO<sub>2</sub>, MgO, CaO and Na<sub>2</sub>O contents are close to calculated values. The results for P<sub>2</sub>O<sub>5</sub> are significantly different and indicate that the behaviour of this element depends on its solubility in graphite or a metallic Fe phase. Symbols: (1) glass compositions calculated assuming that part of the reduced FeO has been removed; (2) the initial FeO content in the glass; (3), (4), (5) compositions of glasses after experiments Fb-148, Fb-150, Fb-231, respectively.

content of these globules to be fixed between 2.4 and 7.5 wt %.

### Infrared spectroscopic study

Doubly polished thick sections were prepared to collect the Fourier transform infrared (FTIR) spectra of the quench products. The thickness of the glasses varied between 80 and 262  $\mu\text{m} \pm 1 \mu\text{m}$ . The IR measurements were performed on an FTIR spectrometer (Magna 550, Nicolet) coupled with an optical–IR microscope (LGIS, Paris). Transmission spectra were obtained using the following conditions: MCT<sub>A</sub> detector, Ge over KBr beam splitter, 8  $\text{cm}^{-1}$  resolution, a mirror velocity of 1.899–3.16  $\text{cm/s}$  and a minimum of 300 scans. The aperture diameter was 100  $\mu\text{m}$ . The observed absorption bands in the FTIR spectra were documented for Fb148-gl, Fb150-gl and Fb231-gl samples and they are reported in Table 2. A typical FTIR spectrum of a C–H-bearing glass is illustrated in Fig. 6a.

*O–H species.* Above 3000  $\text{cm}^{-1}$ , a broad, asymmetric band centred at  $\sim 3520 \text{ cm}^{-1}$  is the most prominent feature in the high-frequency region. This absorption band is due mainly to fundamental OH stretching vibrations of OH groups and H<sub>2</sub>O molecules (Stolper, 1982; Newman *et al.*, 1986). The fundamental bending vibration of H<sub>2</sub>O molecules corresponds to a sharp peak at 1633–1635  $\text{cm}^{-1}$ . The relative proportion of molecular H<sub>2</sub>O and hydroxyl group cannot be given, because the molar absorption coefficients are not known for such uncommon melt compositions. The absorption band near 4129–4138  $\text{cm}^{-1}$  identified in Fb150-gl (Fig. 6b) may represent the stretching vibration of the H<sub>2</sub> molecule (Dianov *et al.*, 2000).

*C–O species.* A weak and broad band centred at  $\sim 2360$ – $2370 \text{ cm}^{-1}$  for Fb148-gl and Fb231-gl (not seen in Fb150-gl) is interpreted as dissolved molecular CO<sub>2</sub>. Dissolved carbonates have characteristic absorption band(s) at  $\sim 1600$ – $1380 \text{ cm}^{-1}$  (Fine & Stolper, 1985). Weak and broad peaks at 1430–1435  $\text{cm}^{-1}$

Table 2: FTIR wavenumber of the different peaks observed and their corresponding absorbance

Sample no.	$d^*$ ( $\mu\text{m}$ )	Wavenumber ( $\text{cm}^{-1}$ )					
		$1430 \pm 3$ $\text{CO}_3^{2-}$	$1633 \pm 3$ $\text{H}_2\text{O}$	$2360\text{--}2380$ $\text{CO}_2$	$3525 \pm 10$ $\text{OH}^- \pm \text{H}_2\text{O}$	$4140 \pm 5$ $\text{H}_2$	$4510 \pm 5$ $\text{OH}^-$
<b>Absorbances</b>							
<i>Clear glass</i>							
Fb148C-002	$180 \pm 5$	0.01	0.48	0.06	saturated	0.009	n.d.
Fb148C-004	$180 \pm 5$	0.01	0.39	0.05	saturated	0.010	n.d.
Fb148-001†	$175 \pm 5$	0.03	0.98	0.02	saturated	0.005	0.019
Fb148-004†	$175 \pm 5$	0.07	1.49	—	saturated	—	0.020
Fb150-007	$80 \pm 5$	—	0.16	0.02	1.33	—	0.010
Fb150-010	$80 \pm 5$	—	0.20	—	1.84	0.003	0.013
Fb150-011	$80 \pm 5$	—	0.14	0.02	1.39	—	0.013
Fb231-012	$262 \pm 3$	0.07	0.59	0.01	saturated	0.014	0.033
Fb231-017	$203 \pm 5$	0.032	0.43	0.07	saturated	0.009	0.020
Fb231-020	$121 \pm 2$	0.014	0.27	0.05	2.44	0.100	0.010
Fb231-023	$241 \pm 1$	—	0.58	0.09	saturated	0.012	0.030
<i>Glass with quench dispersed graphite</i>							
Fb148C-001	$180 \pm 5$	0.009	0.05	0.05	saturated	0.009	n.d.
Fb148-002	$175 \pm 5$	0.01	0.42	0.05	saturated	0.009	0.020
Fb148-003†	$175 \pm 5$	0.07	1.57	—	saturated	0.010	0.020
Fb231-016	$262 \pm 3$	0.03	0.47	0.07	saturated	0.010	0.028
Fb231-024	$241 \pm 1$	—	0.64	0.07	saturated	0.010	0.030
Fb231-022	$121 \pm 2$	0.02	0.24	0.03	2.30	0.010	0.013

\*Thickness of the sample.

†The higher absorbance for  $1633\text{ cm}^{-1}$  compared with other measurements reflects structural re-equilibration of the aluminosilicate melt network during quenching or local heterogeneity in concentration of hydrogen in glass.

observed in Fb150-gl and Fb231-gl and in part of Fb148-gl samples could represent such species.

*Other species.* It would be expected that under reduced conditions, C- and H-components other than molecular  $\text{H}_2\text{O}$ ,  $\text{OH}^-$  and  $\text{CO}_2$ , or carbonate ions could exist in the experimental glasses but cannot be detected by IR spectroscopy. The possible candidates are Si–H, Si–C and C–H. C–H bonds are expected at  $3050\text{--}2850\text{ cm}^{-1}$ , Si–H bonds at  $2250\text{--}2100\text{ cm}^{-1}$  and C–H bonds stretching in dissolved molecular methane or other hydrocarbon groups such as  $-\text{CH}_3$  or  $-\text{CH}_2-$  at  $\sim 2900\text{ cm}^{-1}$  (Pouchert, 1981). However, no such absorption bands were noted in our charges.

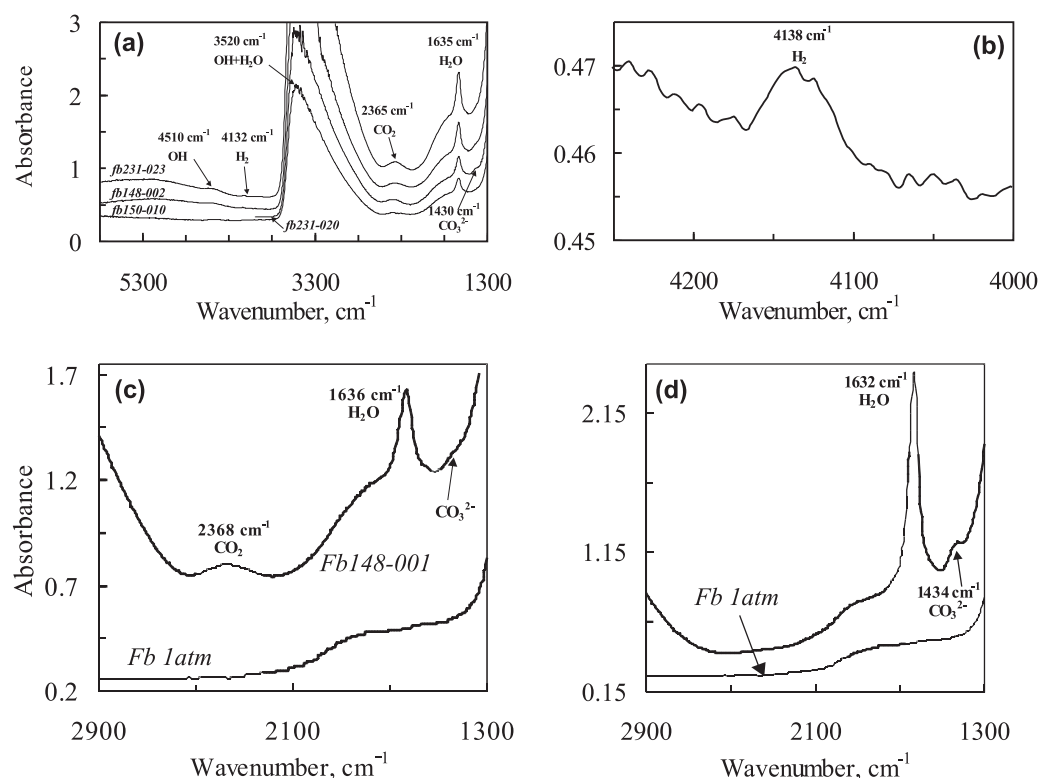
Thus it appears that the main dissolved species correspond to  $\text{OH}^-$  groups. Most of the  $\text{H}_2\text{O}$  content (e.g. between 1 and 2 wt %) certainly occurs in this form. Molecular water is present but the intensity of the signal is low. Molecular  $\text{CO}_2$  and carbonate ions are present only as traces. This means that the carbon content measured by step-heating (see below) is present in a form not detectable by FTIR.

## Raman spectroscopic study

Micro-Raman spectroscopy was used to search for dissolved carbon and hydrogen species in quench glasses and graphite or amorphous carbon. The Raman spectroscopy was performed at the Itodys laboratory at Université de Paris 7–IPGP, using a Dilor XY confocal micro-Raman spectrometer, and at the Institute of General Physics of the Russian Academy of Sciences (Moscow). The spectra were corrected for temperature- and frequency-dependent scattering intensity before statistical analysis. A correction factor of the form employed by Long (1977) and given by Neuville & Mysen (1996) was used. The corrected Raman intensities were normalized to the data point of the greatest absolute intensity.

The Raman spectra of the glasses in the high-frequency region ( $3000\text{--}3800\text{ cm}^{-1}$ ) show a broad, asymmetric band at  $\sim 3560\text{ cm}^{-1}$  (Fig. 7a). The topology of this band is similar to that found for  $\text{H}_2\text{O}$ -bearing glasses by Mysen & Virgo (1986) and for  $\text{H}^-$ -bearing glasses in the system  $\text{Na}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$  by Luth *et al.* (1987). This band is assigned to the stretching vibrations of  $\text{OH}^-$





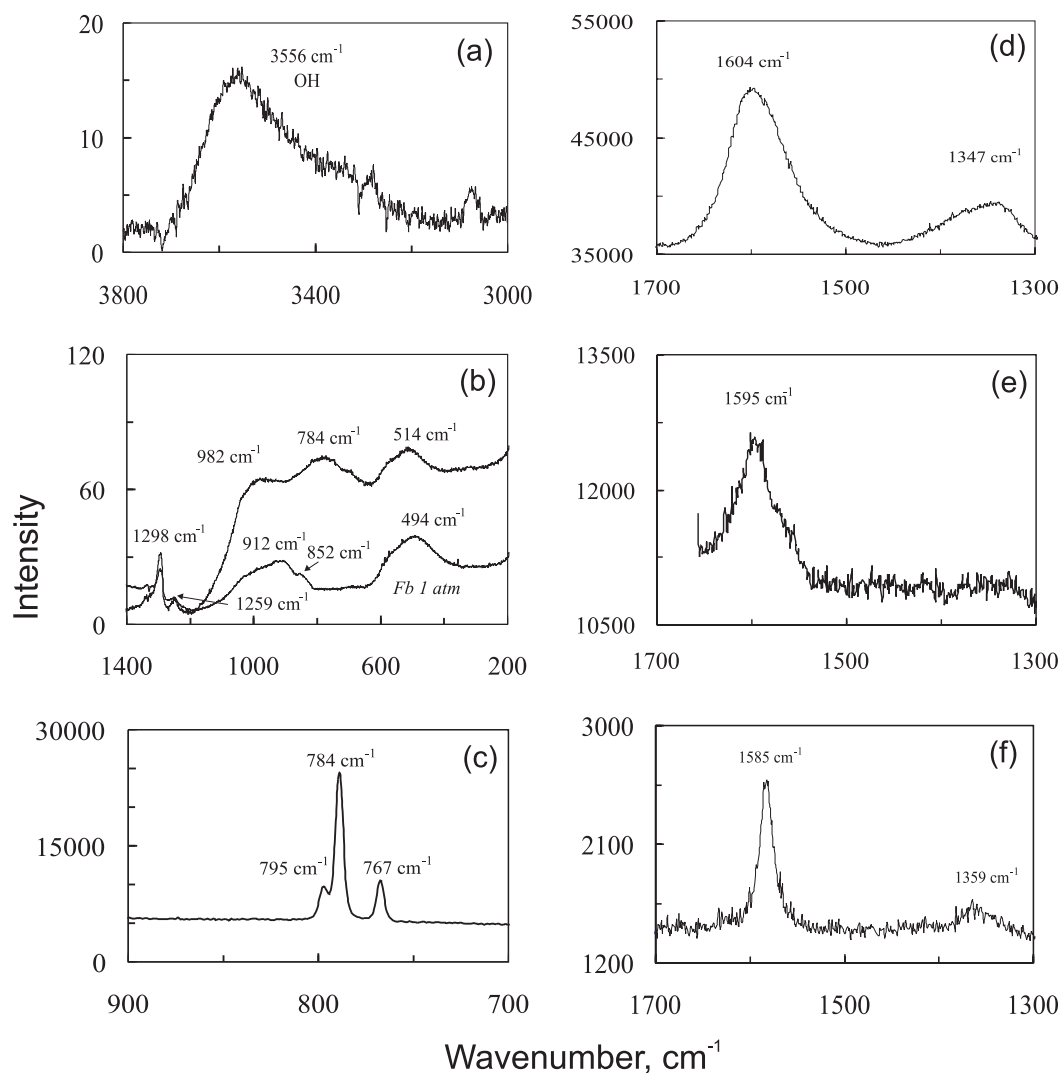
**Fig. 6.** FTIR spectra of H-bearing quenched glasses. (a) FTIR spectra over the range 6000–1300  $\text{cm}^{-1}$  for: the initial ferrobasaltic glass (Fb 1 atm, sample thickness  $40 \pm 2 \mu\text{m}$ ) quenched from 1 atm at  $1300^\circ\text{C}$  and  $\Delta\log f\text{O}_2 = \text{IW} - 2.46 \log$  units; sample Fb148-gl, thickness  $175 \pm 5 \mu\text{m}$ ; Fb150-gl,  $80 \pm 0.5 \mu\text{m}$ ; Fb231-gl,  $121 \pm 2 \mu\text{m}$  and  $241 \pm 1 \mu\text{m}$ . The wide band near  $4500 \text{ cm}^{-1}$  is assigned to the OH group. (b) The absorption band near  $4138 \text{ cm}^{-1}$  (Fb150-gl,  $80 \pm 0.5 \mu\text{m}$ ) corresponds to the vibration of the H–H bond. (c) FTIR spectrum in the range 2900–1300  $\text{cm}^{-1}$  should show the typical vibration of the C–O bond. The initial ferrobasaltic glass (Fb 1 atm, see Fig. 7a) is compared with sample Fb148-001. A broad, weak band centred at  $\sim 2368 \text{ cm}^{-1}$  is interpreted as dissolved molecular  $\text{CO}_2$ . No dissolved carbonate ion was detected. (d) Sample Fb150 shows a weak and broad peak at  $1430\text{--}1435 \text{ cm}^{-1}$  interpreted as dissolved carbonate ion. No dissolved molecular  $\text{CO}_2$  was detected.

groups, either in molecular or in  $\text{OH}^-$  groups bonded to cations in the silicate network.

In the low-frequency region ( $1200\text{--}400 \text{ cm}^{-1}$ ), our glassy samples show distinct bands at  $982 \text{ cm}^{-1}$ ,  $784 \text{ cm}^{-1}$  and  $514 \text{ cm}^{-1}$  (Fig. 7b). These correspond to aluminosilicate band frequencies found in the ranges  $500\text{--}600 \text{ cm}^{-1}$ ,  $800\text{--}850 \text{ cm}^{-1}$  and  $900\text{--}1200 \text{ cm}^{-1}$  (as in all aluminosilicates); however, the frequencies and the intensities of the framework vibration bands depend strongly on glass composition (Neuville & Mysen, 1996; Mysen, 1998). For comparison, the initial glass, quenched from 1 atm,  $1300^\circ\text{C}$  and  $\Delta\log f\text{O}_2^{\text{IW}} = -2.46$  units was the same as during the experiments at 3.7 GPa and  $1520\text{--}1600^\circ\text{C}$ , and the given activities of C and H. As in the high-pressure experiments, the ferrobasaltic melt was reduced with formation of a metallic Fe phase. This sample exhibits four bands at  $1298 \text{ cm}^{-1}$ ,  $1259 \text{ cm}^{-1}$ ,  $912 \text{ cm}^{-1}$  and  $494 \text{ cm}^{-1}$ , similar to the carbon- and hydrogen-bearing glasses, but with decreasing frequencies for the last two. These correspond to aluminosilicate band frequencies (Fig. 7b). In this figure, the sample exposed to 3.7 GPa shows a peak at  $\sim 800 \text{ cm}^{-1}$ . Spectral features of glasses after high-pressure experiments are

considered to represent the influence of hydrogen and carbon on melt structure. For example, Mysen (1998) interpreted the pronounced peak present at  $784 \text{ cm}^{-1}$  as the Si–OH stretching frequency in the framework for the system  $\text{K}_2\text{O}\text{--}\text{SiO}_2\text{--}\text{H}_2\text{O}$ . This vibration peak at  $784 \text{ cm}^{-1}$  can also be assigned to the Si–C band found in moissanite [Debernardi *et al.*, 1999; see also our definitions (Fig. 7c)]. The Raman spectrum we observed for a synthetic moissanite crystal (parallel to the *c*-axis) exhibits two strong bands centred at  $784$  and  $762 \text{ cm}^{-1}$ . This is a strong indication that Si–C may be present in our samples. However, this requires further experimental study.

Broad bands are observed at approximately  $1347 \text{ cm}^{-1}$  and  $1604 \text{ cm}^{-1}$  (Fig. 7d) in spectra taken with the laser beam focused on the black zones in the region of dendritic microstructure (see Fig. 4c and d). These vibrations correspond to poorly crystallized graphite or amorphous carbon (Lespade *et al.*, 1982). Individual crystals of graphite present in clear glass show sharp bands at  $1595 \text{ cm}^{-1}$  and no band around  $1347 \text{ cm}^{-1}$  (Fig. 7e), whereas a graphite disc (located at the top of the sample during the experiment), displays a sharp band at  $1585 \text{ cm}^{-1}$  and a small one at  $1359 \text{ cm}^{-1}$ ; Fig. 7f).



**Fig. 7.** Raman spectra. (a) Fb231-gl: a broad, asymmetric band at  $\sim 3560\text{ cm}^{-1}$  is assigned to the stretching vibrations of the O–H band, either in molecular or hydroxyl groups bonded to the silicate network. (b) Comparison between the low frequency ( $1400\text{--}200\text{ cm}^{-1}$ ) of the carbon- and hydrogen-bearing glasses in Fb 1 atm and Fb231-gl. The pronounced peak at  $784\text{ cm}^{-1}$  is assigned to the Si–OH or Si–C bond. (c) Raman spectra of a synthetic Si–C crystal. (d)–(f) are Raman spectrum of graphite over the range  $1700\text{--}1300\text{ cm}^{-1}$ . (d) Fine dispersed graphite in Fb148-gl. (e) Thin hexagonal tablets of graphite crystal in Fb231-gl. (f) Graphite disc that was located in a top of the sample during experiment (see Fig. 1b).

Following Lespade *et al.* (1982) and Rouzaud *et al.* (1983), bands at  $1347\text{--}1355\text{ cm}^{-1}$  and at  $1585\text{--}1604\text{ cm}^{-1}$  are attributed to the C–C stretching region of graphite with various degrees of crystal order. With increasing disordering, the  $1582\text{ cm}^{-1}$  band broadens and moves to higher frequency, and a broad band appears at  $\sim 1350\text{ cm}^{-1}$  and increases in intensity. According to these observations, the extremely fine dispersed black particles in the region of dendritic microstructure represent poorly crystallized graphite or amorphous carbon.

#### Ion probe analysis of the $^1\text{H}^+ / ^{30}\text{Si}^+$ ratio in the glasses

Polished thin sections were prepared to measure the  $^1\text{H}^+ / ^{30}\text{Si}^+$  ratio in the glasses (sample Fb231-gl) with a

Cameca IMS 3f ion microprobe (Institute of Microelectronics and Informatics, Russian Academy of Sciences, Yaroslavl<sup>1</sup>). Samples were ultrasonically cleaned in pure alcohol, baked at  $40^\circ\text{C}$  overnight, coated with gold, and kept at  $40^\circ\text{C}$  until introduction into the ion microprobe. The intensities on peaks  $^1\text{H}^+$  and  $^{30}\text{Si}^+$  were recorded under bombardment of an  $\text{O}_2^-$  primary beam of  $10\text{--}15\text{ nA}$  intensity and  $10\text{ }\mu\text{m}$  in size, at mass resolution of  $1200$  and with an energy filtering of  $100 \pm 20\text{ V}$ .  $\text{H}_2\text{O}$  contents of  $1.65 \pm 0.03\text{ wt \%}$   $\text{H}_2\text{O}$  were obtained using the calibration curves of Sobolev & Chaussidon (1996). Those workers have calibrated the  $^1\text{H}^+ / ^{30}\text{Si}^+$  ratios versus the  $\text{wt \% H}_2\text{O} / \text{wt \% SiO}_2$  ratios in the range  $0.09\text{--}8\text{ wt \% H}_2\text{O}$ . No strong matrix effects were found on standards ranging in  $\text{SiO}_2$  content between  $49$  and

71 wt %. It is necessary to note that our experiment has been carried out at low  $fO_2$  and the hydrogen in the glasses can exist in other forms than  $H_2O$ . Consequently, the  $H_2O$  contents should be considered as maximum values.

### Step-heating extraction under oxidizing conditions

During step-heating extraction, the sample is heated under a moderate oxygen pressure. The temperature is chosen in such a way that it corresponds to the extraction of given carbon species (see Pineau & Javoy, 1994, for details). In mid-ocean ridge basalt-type glassy samples the carbon extracted above 900°C is considered to represent the carbon dissolved in the glass (mainly present in the form of carbonate ions). The entire  $H_2O$  content is extracted between 200°C and melting temperature (usually 1300–1350°C). Each carbon fraction (in the form of  $CO_2$ ) and  $H_2$  was isotopically analysed on a Finnigan Mat delta E mass spectrometer with appropriate blank corrections.

Two samples (Fb148-gl and Fb150-gl) were studied. The first one is composed of the glassy fraction still coated on one side by part of the graphite disc. The second had this graphite removed by a careful polishing. To burn the graphite present in sample Fb148-gl, the 900°C step was repeated until the amount of carbon came close to the blank value. Then, a single step at 1300°C extracted the remaining carbon. The amount of carbon and water extracted at each temperature step and the corresponding isotopic composition are given in Table 3. Several comments can be made. (1) During the two experiments, the  $H_2O$  was extracted during the 900°C step, and the amounts vary by a factor of two ( $1.0 \pm 0.1$  and  $2.01 \pm 0.05$  wt % in Fb148-gl and Fb150-gl, respectively). The  $\delta D$  values of the water extracted from both samples are similar ( $-123$  and  $-133\text{‰}$ ). The preparation of sample Fb150-gl (graphite elimination by polishing) may have introduced some water, not removed by the degassing step. Nevertheless, this adsorbed water should have been expressed mainly at 650°C, whereas it represents only 10% of the total water extracted. It is difficult to consider that in one case the water is inherited from the experiments and in the other it comes from an external polluting product, whereas both have the same isotopic composition. Consequently, it is considered that both measurements are correct and the variations between them are linked to heterogeneity inside the samples. (2) Sample Fb150-gl does not contain the graphite disc. The oxidation of the glass at the 650°C step is slow and corresponds in part to cleaning. Consequently, it has not been taken into consideration. On the contrary, half of the total carbon is already extracted at 900°C (in three steps) and the other half at 1300°C, which means that the

*Table 3: Carbon, water, and nitrogen concentration, and  $\delta^{13}C$  and  $\delta D$  in samples Fb148-gl and Fb150-gl by step-heating experiments*

Sample number:	Fb148-gl		Fb150-gl		
Glass weight:	0.060 g		0.109 g		
Temperature:	900°C	1300°C	650°C	900°C	1350°C
Number of steps:	4	1	2	3	1
<hr/>					
$CO_2$					
μmoles	1297	3.56	0.4	7.4	7.5
ppm C	1045*	46		813	826
$\delta^{13}C$	-26.4	-26.6	-28.3	-27.7	-26.9
$H_2O$					
μmoles	25	<blank	10	102	<blank
wt %	1.01	2.01			
$\delta D$		-123‰			-133‰
$N_2$					
μmoles		0.15			
ppm $N_2$		270			

\*Water and carbon concentrations have been calculated using the glass weight (= starting sample weight – graphite weight calculated).

The precisions on concentrations are  $\leq \pm 10\%$  for carbon,  $\leq \pm 5\%$  for water and about 20% for nitrogen. The precisions on  $\delta^{13}C$  are  $\pm 0.02$  for graphite (analytical precision); 0.1–0.2‰. For high-temperature steps;  $\pm 2\%$  on  $\delta D$ .

reduced glass is oxidized at 900°C and that the reduced carbon content, seen by Raman exploration, is liberated in the form of  $CO_2$  as a result of the presence of the 4 mbar oxygen pressure. The 1639 ppm C extracted from sample Fb150-gl corresponds to the sum of the 900 and 1300°C steps.

When a graphite disc is present (Fb148-gl), a rather long oxidation at 900°C is needed (210 min). During the first three 900°C steps, the oxygen is used to burn the graphite; however, during the fourth combustion step, when most graphite has already gone, part of the oxygen may oxidize the reduced glass and part of the amorphous carbon may be extracted. Nevertheless, 1045 ppm of carbon was extracted during the 1300°C step. This represents 63% of the carbon extracted from Fb150-gl.

The H/C atomic ratios are very similar, 14.04 and 13.69 for Fb150-gl and Fb148-gl, respectively. This is consistent with the possibility that the samples are heterogeneous (otherwise, there would be no reason to preserve the H/C ratio). This means that when the water content increases the dissolved carbon content also increases. This is an important result, indicating that the behaviour of the two elements (C and H) is closely related and certainly linked to the opposite effects of

water (depolymerization) and carbon (polymerization) on the silicate network.

The carbon isotopic composition was measured (see Table 2). The  $\delta^{13}\text{C}$  of the starting graphite was  $-26.5 \pm 0.1\text{‰}$ . In Fb150-gl, it is a little lighter ( $-27.3\text{‰}$ ), whereas it is identical for Fb148-gl ( $-26.6\text{‰}$ ). The relationship between these two values is explained by a loss of  $\text{CO}_2$  (enriched in  $^{13}\text{C}$ ) during the last oxidation step at  $900^\circ\text{C}$ . The isotopic difference observed between the graphite of the disc and the carbon present in Fb150-gl gives a first measurement of the isotopic fractionation between these two carbon phases of  $0.8\text{‰}$ .

## DISCUSSION

### Comparison with previous studies

The mean  $\text{H}_2\text{O}$  contents deduced from ion microprobe analysis ( $1.65\text{ wt } \%$ ) and by stepwise heating experiments ( $1\text{--}2\text{ wt } \%$ ) are compatible with the amount of oxygen liberated during the reduction of the ferrobaltic melt to form the Fe metallic phase and equal to  $1.96\text{ wt } \%$   $\text{H}_2\text{O}$  for Fb150-gl and  $1.83\text{ wt } \%$   $\text{H}_2\text{O}$  for Fb231-gl. These values are at the lower limit of the  $1.7 \pm 0.1$  to  $4.8\text{ wt } \%$   $\text{H}_2\text{O}$  (Taylor & Green, 1987) in soda-melilite and jadeite glasses respectively, equilibrated with a methane-rich fluid ( $3\text{ GPa}$ ,  $1300^\circ\text{C}$ ,  $\Delta\log f\text{O}_2^{\text{IW}} = -5$ ). Such glasses contained between  $0.1$  and  $0.2\text{ wt } \%$  of carbon, which is also compatible with the amount of carbon found in our reduced ferrobaltics and in alkali and tholeiitic basalts with a  $\text{CH}_4$ -dominated fluid at  $1\text{--}2\text{ GPa}$  and  $1200^\circ\text{C}$ , buffered by graphite, iron and wüstite (Holloway & Jakobsson, 1986). In the later case,  $3.7\text{--}4.8\text{ wt } \%$   $\text{H}_2\text{O}$  was found, which is two to three times higher than in our samples. This may be explained by the absence of a significant degree of reduction (the reduction of the melt being controlled by hydrogen diffusion through the Pt capsule).

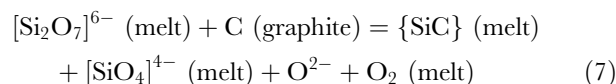
Under more oxidizing conditions, the solubilities of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are much higher than those found in the present study. For example, Pan *et al.* (1991) found that  $3350\text{ ppm C}$  in basaltic melt equilibrated with  $\text{CO}_2$  at  $15\text{ GPa}$  and  $1400\text{--}1600^\circ\text{C}$ ; Dixon *et al.* (1995) and Pineau *et al.* (1998) found up to  $8.3\text{--}8.6\text{ wt } \%$   $\text{H}_2\text{O}$  at  $0.5\text{ GPa}$  and  $1200\text{--}1250^\circ\text{C}$  in basalt and basaltic andesite. All these results suggest that C and H solubility increases when the  $f\text{O}_2$  in the C–O–H system changes from IW or below to  $\sim\text{FMQ}$ .

### Mechanisms of C and H dissolution

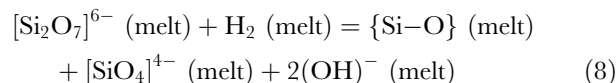
Eggler & Baker (1982), Holloway & Jakobsson (1986), Luth *et al.* (1987) and Taylor & Green (1987) have shown that equilibration of a silicate melt with a  $\text{CH}_4$ -,  $\text{H}_2$ -bearing fluid phase causes a reduction of the silicate network to give an 'oxidized bond' such as O–H or

O–C. Under  $f\text{O}_2$  equivalent conditions, but without a  $\text{CH}_4$ - and  $\text{H}_2$ -rich phase, the behaviour of C and H seems to diverge. Our data indicate that in the presence of graphite the slow and continuous introduction of hydrogen reduces FeO and forms an 'oxidized' hydrogen component, dominantly  $\text{OH}^-$  and, to a lesser extent,  $\text{H}_2\text{O}$ . The predominance of the  $\text{OH}^-$  group over  $\text{H}_2\text{O}$  may indicate the possible presence of molecular  $\text{H}_2$ . For example, Luth *et al.* (1987) have detected the presence of molecular  $\text{H}_2$  in hydrous glasses in the system  $\text{Na}_2\text{O}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2\text{--}\text{H}_2$ .

Rather small amounts of carbon can be dissolved in the melt in a neutral form (atomic carbon?), possibly forming amorphous C during quenching, with trace amounts of  $\text{CO}_2$  and  $\text{CO}_3^{2-}$ . The spectroscopic data indicate the beginning of the silicate network reduction, with the formation of Si–C bonds. Such a reduction of the silicate network can become more important as the reduction process progresses and will favour the formation of a non-stoichiometric network component containing units with an O/Si ratio  $< 2$ . The formation of Si–C bonds can be described by the following equation for  $[\text{Si}_2\text{O}_7]^{6-}$ :



and



where  $\{ \}$  represents an unidentified location in the silicate network and  $[ \ ]$  a melt-unit or complex.

These reactions correspond to a network depolymerization by a change in the activity of network-modifying oxides (Taylor & Green, 1987), which may influence the viscosity and density of the melt.

### The transport of volatile constituents in the Earth

The transport of volatile constituents from planetary interiors to their surface may provide an important part of the atmosphere and hydrosphere, the rest being provided by late additions (late veneer). It is generally agreed that, on terrestrial planets, this transport is strongly dependent on the solubility of the volatile species in magmas. Our experiments on the reduction of a ferrobaltic by an influx of hydrogen in the presence of graphite is an attempt to mimic some transition stages during the melting event produced by a great impactor which is commonly invoked in Earth formation models (e.g. Javoy, 1998, 1999). The magmas formed during this event would have had a composition varying from ferroan komatiites to reduced ferrobaltic. The  $\text{H}_2$  present in the primitive Earth body (corresponding to

~400–500 ppm ‘virtual’ H<sub>2</sub>O if oxidized) would have reduced the FeO to produce OH groups dissolved in the melt whereas graphite would remain stable under these conditions. This is a simple way to explain the formation of the atmosphere–hydrosphere system outgassed from the reduced primitive Earth. When the late, more oxidized, volatile additions (late veneer) started to be recycled, the magmas would become more and more oxidized and dissolve more water and carbon (in the form of carbonate ions).

## CONCLUSIONS

It has been demonstrated that the interaction between a graphite–hydrogen system and Fe-bearing melt (ferrobasalt) at 3.7 GPa, 1520–1600°C and  $fO_2 = IW - 2.5$  generates a general reduction of the silicate melt and C and H dissolution by the formation of C–O–H volatile species.

Under our experimental conditions, hydrogen appears much more reactive than carbon, and forms dissolved OH<sup>−</sup>, H<sub>2</sub>O, and H<sub>2</sub>. Carbon is mainly dissolved in the melt as amorphous or atomic C. The excess of C is expressed as well-crystallized graphite in equilibrium with the melt. It is possible that transitional oxidized forms of C exist. An isotopic fractionation of 0.8‰ was measured between graphite and dissolved or amorphous carbon for a temperature of  $1560 \pm 40^\circ\text{C}$ .

The existence of silicon–carbon bonds is proposed, with the possible consequence of a depolymerization of the silicate network and changes in the activity of network-modifying oxides.

The amounts of C–O–H volatile dissolved in melts at low  $fO_2$  and 3.7 GPa (corresponding to ~100 km depth in the mantle) are particularly low. Carbon solubility is about an order of magnitude less than that of H<sub>2</sub>O (about 2 wt % H<sub>2</sub>O and 0.2 wt % C).

These conclusions confirm the earlier works of Holloway & Jakobsson (1986) and Taylor & Green (1987), showing the dissolution of CH<sub>4</sub> in reduced silicate melts to be associated with H<sub>2</sub>O and OH formation (from  $\log fO_2 = IW$  to  $\log fO_2 = IW - 5$  log units). Similar to the work of Taylor & Green (1987), which was carried out at lower  $fO_2$  ( $fO_2 = IW - 5$  log units) and 3 GPa (on jadeite and soda-melilite compositions), we did not detect the presence of dissolved carbonate ion in the experimental melts. The formation of CO<sub>3</sub><sup>2−</sup> and CO<sub>2</sub> in basic magmas at  $fO_2$  values below the IW oxygen buffer seems to require higher  $fO_2$  values than that of H<sub>2</sub>O and OH species or a depletion of hydrogen in the starting material.

In conclusion, it appears that the chemical evolution of carbon and hydrogen during the very reduced episode of early mantle evolution could be very much influenced by the presence of iron-rich melts. The iron reduction in

these melts is a way of providing the transformation of the reduced forms of hydrogen and carbon that were present in the early mantle (e.g. Javoy 1995, 1997, 1999) into the now dominant mantle forms (hydroxyl group, molecular water and carbonate ion).

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## REFERENCES

- Arculus, R. J. (1985). Oxidation status of the mantle: past and present. *Annual Review of Earth and Planetary Sciences* **13**, 75–95.
- Arculus, R. J., Holmes, R. D., Powell, R. & Richter, K. (1990). Metal–silicate equilibria and core formation. In: Newsom, H. E. & Jones, J. H. (eds) *Origin of the Earth*. Houston, TX: Lunar and Planetary Institute; New York: Oxford University Press, pp. 251–271.
- Ariskin, A. A., Borisov, A. A. & Barmina, G. S. (1993) Simulating iron–silicate melt equilibrium in basaltic systems. *Geochemistry International* **30**, 13–22.
- Ballhaus, C. (1993). Redox states of lithospheric and asthenospheric upper mantle. *Contributions to Mineralogy and Petrology* **114**, 331–348.
- Ballhaus, C. (1995). Is upper mantle metal-saturated? *Earth and Planetary Science Letters* **132**, 75–86.
- Bohlen, S. R. & Boettcher, A. L. (1982). The quartz–coesite transformation: a precise determination and the effects of other components. *Journal of Geophysical Research* **87**, 7073.
- Chou, I.-M. (1987). The oxygen buffer and hydrogen sensor techniques at elevated pressures and temperatures. In: Ulmer, G. C. & Baren, H. L. (eds) *Hydrothermal Experimental Techniques*. John Wiley, New York, pp. 61–99.
- Daniels, L. R. M. & Gurney, J. J. (1991). Oxygen fugacity constraints on the southern African lithosphere. *Contributions to Mineralogy and Petrology* **108**, 154–161.
- Debernardi, A., Ulrich, C., Syassen, K. & Cardona, M. (1999). Raman linewidths of optical phonons in 3C–SiC under pressure: first-principles calculations and experimental results. *Physical Review B* **59**(10), 6774–6783.
- Dianov, E. M., Bubnov, M. M., Gurianov, A. N., Hopin, V. F., Kryukova, E. B., Plotnichenko, V. G., Rybaltovskii, A. A. & Sokolov, V. O. (2000). Phosphosilicate glass optical fibres—a promising material for Raman lasers. *Proceedings of ECOC 2000, 3–7 September, Munich*, **3**, pp. 135–136.

- Dixon, J. E., Stolper, E. M. & Holloway, J. R. (1995). An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. I. Calibration and solubility models. *Journal of Petrology* **36**, 1607–1631.
- Eggler, D. H. & Baker, D. (1982). Reduced volatiles in the system C–O–H: implications to mantle melting, fluid formation, and diamond genesis. In: Akimoto, S. & Manghni, M. (eds) *High Pressure Research in Geophysics*. Tokyo: Center for Academic Publications, pp. 237–250.
- Fine, G. & Stolper, E. (1985). The speciation of carbon dioxide in sodium aluminosilicate glasses. *Contributions to Mineralogy and Petrology* **91**, 105–121.
- Galimov, E. M. (1998). Growth of the Earth's core as a source of its internal energy and a factor of mantle redox evolution. *Geochemistry International* **36**, 673–675.
- Hillgren, V. J., Drake, M. J. & Rubie, D. C. (1994). High pressure and temperature experiments on core–mantle segregation in the accreting Earth. *Science* **264**, 1442–1445.
- Holloway, J. R. (1981). Volatile interactions in magmas. In: Newton, R. S., Navrotsky, A. & Wood, B. J. (eds) *Thermodynamics of Minerals and Melts*. Advances in Physical Geochemistry, 273–293.
- Holloway, J. R. & Jakobsson, S. (1986). Volatile solubilities in magmas: transport of volatiles from mantles to planet surface. *Journal of Geophysical Research* **91**(B4), D505–D508.
- Holloway, J. R., Pan, V. & Gudmundsson, G. (1992). High-pressure fluid-absent melting experiments in the presence of graphite: oxygen fugacity, ferric/ferrous ratio and dissolved CO<sub>2</sub>. *European Journal of Mineralogy* **4**, 105–114.
- Javoy, M. (1995). The integral Enstatite Chondrite model of the Earth. *Geophysical Research Letters* **22**, 2219–2222.
- Javoy, M. (1997). The major volatile elements of the Earth: origin, behavior, and fate. *Geophysical Research Letters* **24**, 177–180.
- Javoy, M. (1998). The birth of the Earth's atmosphere: the behaviour and fate of the major elements. *Chemical Geology* **147**, 11–25.
- Javoy, M. (1999). Chemical Earth model. *Comptes Rendus de l'Académie des Sciences, Sciences de la Terre et des Planètes* **329**, 537–555.
- Kadik, A. A. (1996). Formation of carbon species in terrestrial magmas. In: Farley, K. A. (ed.) *Volatiles in the Earth and Solar System*. American Institute of Physics Conference Proceedings **341**, 106–114.
- Kadik, A. A. (1997). Evolution of Earth's redox state during upwelling of carbon-bearing mantle. *Physics of the Earth and Planetary Interiors* **100**, 157–166.
- Lespade, P., Al-Jishi, R. & Dresselhaus, M. S. (1982). Model for Raman scattering from incompletely graphitized carbons. *Carbon* **5**, 427–431.
- Litvin, Yu. A. (1989). On the technique of high-pressure studying phase equilibrium of ferro-ferrous magmatic melts. *Geochimia* (8), 1234–1242 (in Russian).
- Long, D. A. (1977). *Raman Spectroscopy*. New York: McGraw–Hill, 276 pp.
- Luth, R. W., Mysen, B. O. & Virgo, D. (1987). Raman spectroscopic study of the solubility behavior of H<sub>2</sub> in the system Na<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>. *American Mineralogist* **72**, 481–486.
- Mattioli, G. S., Baker, B., Rutter, M. G. & Stolper, E. M. (1989). Upper mantle oxygen fugacity and relationship to metasomatism. *Journal of Geology* **97**, 521–536.
- Mysen, B. O. (1998). Interaction between aqueous fluid and silicate melt in the pressure and temperature regime of the Earth's crust and upper mantle. *Neues Jahrbuch für Mineralogie, Abhandlungen* **172**(2–3), 227–244.
- Mysen, B. O. & Virgo, D. (1986). Volatiles in silicate melts at high pressure and temperature, 2. Water in melts along the join NaAlO<sub>2</sub>–SiO<sub>2</sub> and a comparison of solubility mechanisms of water and fluorine. *Chemical Geology* **57**, 333–358.
- Neuville, D. R. & Mysen, B. O. (1996). Role of aluminium in the silicate network: *in situ*, high-temperature study of glasses and melts on the joint SiO<sub>2</sub>–NaAlO<sub>2</sub>. *Geochimica et Cosmochimica Acta* **60**, 1727–1737.
- Newman, S., Stolper, E. M. & Epstein, S. (1986). Measurement of water in rhyolitic glasses: calibration of an infrared spectroscopic technique. *American Mineralogist* **71**, 1527–1541.
- O'Neill, H. St. C. (1991). The origin of the Moon and the early history of the Earth—a chemical model. Part 2: The Earth. *Geochimica et Cosmochimica Acta* **55**, 1159–1172.
- O'Neill, H. St. C. & Pownceby, M. I. (1993). Thermodynamic data from redox reactions at high temperatures. I. An experimental and theoretical assessment of the electrochemical method using stabilized zirconia electrolytes, with revised values for the Fe–FeO, Co–CoO, Ni–NiO and Cu–Cu<sub>2</sub>O oxygen buffers, and new data for the W–WO<sub>2</sub> buffer. *Contributions to Mineralogy and Petrology* **114**, 296–314.
- O'Neill, H. St. C. & Wall, V. J. (1987). The olivine–orthopyroxene–spinel oxygen geobarometer, the nickel precipitation curve and the oxygen fugacity of the Earth's upper mantle. *Journal of Petrology* **28**, 1169–1191.
- Pan, V., Holloway, J. R. & Hervig, R. L. (1991). The pressure and temperature dependence of carbon dioxide solubility in tholeiitic basalt melts. *Geochimica et Cosmochimica Acta* **55**, 1587–1595.
- Parkinson, I. J. & Arculus, R. J. (1999). The redox state of subduction zones: insights from arc-peridotites. *Chemical Geology* **166**, 409–423.
- Pineau, F. & Javoy, M. (1994). Strong degassing at ridge crests: the behavior of dissolved carbon and water in basalt glasses at 14°N, Mid-Atlantic Ridge. *Earth and Planetary Science Letters* **123**, 179–198.
- Pineau, F., Shilobreeva, S., Kadik, A. & Javoy, M. (1998). Water solubility and D/H fractionation in the system basaltic andesite–H<sub>2</sub>O at 1250°C and between 0.5 and 3 kbars. *Chemical Geology* **147**, 173–184.
- Pouchert, C. G. (1981). *The Aldrich Library of Infrared Spectra*, 3rd edn. Milwaukee, WI: Aldrich Chemical Co., 1203 pp.
- Rouzaud, J. N., Oberelin, A. & Beny-Badde, C. (1983). Carbon films structure and microtexture (optical and electron microscopy, Raman spectroscopy). *Thin Solid Films* **105**, 75–96.
- Sobolev, A. V. & Chaussidon, M. (1996). H<sub>2</sub>O concentrations in primary melts from supra-subduction zones and mid-oceanic ridges: implications for H<sub>2</sub>O storage and recycling in the mantle. *Earth and Planetary Science Letters* **137**, 45–55.
- Stolper, E. (1982). The speciation of water in silicate melts. *Geochimica et Cosmochimica Acta* **46**, 2609–2620.
- Swisher, J. H. (1968). Thermodynamics of carbides formation and graphite solubility in the CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> system. *Transactions of the Metallurgical Society of AIME* **242**, 2033–2037.
- Taylor, W. R. & Foley, S. F. (1989). Improved oxygen-buffering techniques for C–O–H fluid-saturated experiments at high pressure. *Geophysical Research Letters* **94**(B4), 4146–4158.
- Taylor, W. R. & Green, D. H. (1987). The petrogenetic role of methane: effect on liquidus phase relations and the solubility mechanism of reduced C–H volatiles. In: Mysen, B. O. (ed.) *Magmatic Processes: Physicochemical Principles*. Geochemical Society, Special Publications **1**, 121–138.
- Ulmer, P. & Luth, R. W. (1991). The graphite–COH fluid equilibrium in *P*, *T*, *f*O<sub>2</sub> space. An experimental determination to 30 kbar and 1600°C. *Contributions to Mineralogy and Petrology* **106**, 265.
- Wanke, H. (1981). Constitution of terrestrial planets. *Philosophical Transactions of the Royal Society of London, Series A* **303**, 287–302.
- Wood, B. J. (1995). Storage and recycling of H<sub>2</sub>O and CO<sub>2</sub> in the Earth. In: Farley, K. A. (ed.) *Volatiles in the Earth and Planetary Solar System*. American Institute of Physics Conference Proceedings **341**, 3–21.
- Wood, B. J., Bryndzia, L. T. & Johnson, K. E. (1990). Mantle oxidation state and its relationship to tectonic environment and fluid speciation. *Science* **248**, 337–345.